USE OF CERIUM (IV) SALTS IN ORGANIC OXIDATION PROCESSES

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On the basis of theoretical considerations the possibility of using cerium (IV) salts in organic oxidation processes arose.

Up to the present, cerium (IV) salts had been sporadically applied for preparative purposes in organic oxidation processes. However, their general use in organic oxidation processes seems to be promising since

1. oxidation by these agents proceeds in one step, thus, under given conditions, the reaction can be easily controlled,
2. the redox potential of the agents is high,
3. the rate of oxidation can be varied within broad limits by changing the nature of salt and acid, further by varying the concentration of acid applied,
4. processes may be promoted by ultraviolet light, facilitating by this way any oxidative operations under mild conditions,
5. it is possible to apply other catalysts as well,
6. the bond $>C=C<$ is resistant against the agents,
7. no decarboxylation was observed, even when brutal experimental conditions were applied,
8. also a selective oxidative action may be secured in the simultaneous presence of several functional groups.

Experiments conducted so far by the authors confirmed the above conclusions drawn from literature data. Data of these experiments will be discussed in a next paper.

Organic oxidation processes may be classified on the basis of their progress in three groups [1]:

1. Delivery of oxygen,
2. Uptake of hydrogen,
3. Uptake of electrons.

Certain oxidation processes as *e. g.* the oxidation of ethanol to acetaldehyde may be interpreted by direct oxidation as well as by the WIELAND theory of dehydrogenation [2]. Ionic oxidizing agents may be considered as substances taking up electrons [3]. Numerous representatives of this latter group are often used in organic chemistry as oxidizing agents. In the present communication, the suitability of cerium (IV) salts so far almost neglected in the practice of organic preparative work will be discussed.

The use of cerium (IV) salts in organic oxidation processes seems practical, since

1. cerium is a one-step oxidizing agent:

$$Ce^{4+} + e \rightarrow Ce^{3+}$$

thus, it may be expected that the oxidation process can easier be controlled than in the case of multiple electron leaps, as *e.g.* with permanganate:

$$MnO_4^- + 8H^+ + 5e \rightarrow Mn^{2+} + 4H_2O.$$

2. the system cerium (IV)-cerium (III) has a high redox normal potential.

The prerequisite of the progress of an oxidation process is that the redox potential of the ionic oxidizing agent determined by the equation

$$E = E_0 + \frac{RT}{nF} \ln \frac{C_{ox} \cdot f_{ox}}{C_{red} \cdot f_{red}}$$

should exceed the redox potential and, respectively, the apparent redox potential of the organic substance [4], [5].

Numerous research workers dealt with the redox potential of the system cerium (IV)-cerium (III) in the case of various salts and acids [6]—[9]. It was found [10] that the maximum redox potential of the system cerium (IV)-cerium (III) appears with $Ce(ClO_4)_4$—$HClO_4$.

1-8 N solution of $HClO_4$	$E = 1{,}70$-$1{,}87$ V.
1-8 N solution of HNO_3	$E = 1{,}61$-$1{,}56$ V.
1-8 N solution of H_2SO_4	$E = 1{,}44$-$1{,}42$ V.
1 N solution of HCl	$E = 1{,}28$ V.

This observation was later interpreted theoretically as well [11]—[13].

While the redox potential of $Ce(SO_4)_2$ changes but slightly from 8 N H_2SO_4 to pH 1, a quick decrease appears with rising values of pH [14]

pH	1	1,95	3,05	4,00	4,90	6,10	7,70	9,10	9,55
E	1,460	1,401	1,357	1,154	0,898	0,607	0,320	0,217	0,163 V

These data show that potential values determining the course of the oxidation reaction may be varied between extremely broad limits by selecting adequate salts and acids, respectively, and by varying the concentration of acid.

3. applicability of catalysts.

In addition to the above mentioned factors, there exist also other ones affecting the rate of the oxidation processes carried out with the use of cerium (IV) salts. Certain authors are of the opinion [15]—[17] that rare earth contaminations present in cerium salts do not influence the rate of the oxidation reaction. However, it was recently stated that the presence of chromic sulphate catalyses the process [18].

In certain ionic reactions the rate of reaction is appreciably reduced by the presence of cerium (III) salts [19].

Osmium tetroxide [20] and iodine monochloride [21] are often applied as catalysts. The promoting action of ultraviolet light on oxidation reactions of this type has also been observed [22]—[26].

On taking all these facts into consideration, it is possible to conduct oxidation reactions under extremely mild conditions.

In the next chapters a survey is given of organic cerimetric determinations and kinetical investigations which may serve as a basis for drawing conclusions as regards reactions which may be carried out and experimental conditions affecting these reactions. Finally the sporadical cases of application in preparative operations will also be mentioned.

Analytical applications

Cerium (IV) salts are extensively used for analytical purposes. LANGE [27] proposed the application of cerium (IV) sulphate as a measuring solution as early as in 1861. However, the wide-spread use in inorganic quantitative analysis began only at about 1900, as a consequence of the observation of JOB published in 1899 [28] according to whom $Ce(SO_4)_2$ is resistant againts potassium permanganate even in an acid medium.

Application of cerium salts for the quantitative determination of organic substances appears to be rather new. A general feature of these methods [29] is to use an excess of cerium (IV) and to oxidize the organic molecules to carbon dioxide, formic acid and water, or quite recently [30], [31] splitting formic acid as well into carbon dioxide and water, and measuring the excess of cerium by titration.

BENRATH and RULAND determined in 1920 various organic acids with the use of $Ce(SO_4)_2$ [15] and found that by raising the concentration of H_2SO_4 or adding neutral sulphates, the rate of the oxidation reaction is reduced in the case of tartaric, oxalic, malonic and citric acids (cf. Table I).

Table I

0,20 g tartaric acid, 1,826 g $Ce(SO_4)_2$ in 150 ml water

Quantity of H_2SO_4	Duration of reaction
1,104 g = X	22 minutes
3 X	30 minutes
4 X	39 minutes
6 X	62 minutes
10 X	142 minutes
20 X	no reaction in 360 minutes

With anthracene, however, the reaction was promoted by raising the concentration of sulphuric acid (cf. Table II).

Table II

50 ml of sulphuric acid of various concentration + 1 g of anthracene + 20 ml of 0,1 N $Ce(SO_4)_2$ at room temperature under continuous stirring:

Concentration of H_2SO_4	Duration of reaction
10%	12 hours
20%	6 hours
30%	4 hours
52%	10 minutes!

The increase of concentration of sulphuric acid promoted the oxidation process also with formic, fumaric and maleinic acids. Oxidation can be carried out solely in an acid medium, due to the correlation of the potential of the system $Ce^{4+}—Ce^{3+}$ with pH values and to the solubility of cerium

salts [32], [33]. According to KOLTHOFF, a medium containing 0,5—1,0 N acid is most suitable [34]. Namely, numerous compounds which are readily oxidized under the given conditions of acidity, yield precipitates at lower acidity values [35]—[38] or form complexes with Ce^{4+} ions [39]—[41].

The specific oxidizing action of $Ce(SO_4)_2$ follows from the observation of WILLARD and YOUNG [42] that fumaric and maleinic acids, readily oxidized by $KMnO_4$, proved to be resistant to $Ce(SO_4)_2$ even under relatively brutal experimental conditions whereas benzoic acid, resistant to other oxidizing agents, was readily decomposed by $Ce(SO_4)_2$. WILLARD and YOUNG applied boiling for 30 minutes in a medium of 10—30% sulphuric acid. Under these conditions only a negligible portion of maleinic or fumaric acid present may have reacted.

FURMAN and WALLACE [43] determined in 1930 hydroquinone by oxidation to quinone. As they set the aim to stop the reaction at a given stage of oxidation, titration in the presence of a redox indicator was carried out.

The reaction proceeds as well to the presumed quinone state in the case of oxidizing leuco-malachite green with $Ce(SO_4)_2$ [44]. It seems worth to mention the GORDON method of determining lactic acid [45] according to the equation:

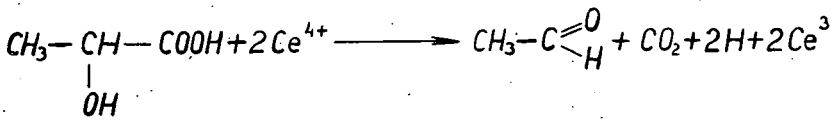

Fig. 1

By this method, 0,4 mg lactic acid may be determined with a mean error ranging below 5%. During the course of these reactions, from practical point of view, no side reactions occur. This feature encourages the ever spreading use of cerium (IV) salts in organic analysis [46]—[49].

Kinetical investigations

The kinetics of the oxidation of aliphatic alcohols by $Ce(SO_4)_2$ was studied by FROMAGEOT [50]. The oxidation of 2,3-butandiol [51] and ethanol [52] to acetaldehyde under the action of $Ce(ClO_4)_4$ was investigated but recently. BENRATH pointed out [15] the catalytic action of ultraviolet light in the oxidation process of alcohols.

On examining the kinetics of the oxidation of acetaldehyde and of aliphatic ketones with the use of $Ce(SO_4)_2$, SHORTER and HINSHELWOOD found [17], [53] that the capability of enolization is closely correlated with oxidability.

CONANT and ASTON [54] oxidizing iso-butyraldehyde with $Ce(SO_4)_2$, observed that mainly α-oxidation affording α-hydroxy-isobutyraldehyde takes place whereas the expected isobutyric acid formed only in 20%.

Further, the photochemical and kinetical investigations emphasizing the vigorous catalytic action of ultraviolet light, should not be neglected, since the application of this latter is wide-spread in the determination of various organic substances [55]—[58].

Use in preparative operations

In certain cases of electrolytic oxidation, minute amounts (about 2%) of cerium (IV) salts are added as oxygen transmitters [59].

This process may be interpreted by presuming that Ce (IV) is reduced when it oxidizes the organic molecule, to be re-oxidized anodically [60]. *E. g.* an anthracene suspension is electrolytically oxidized in a medium of 30% H_2SO_4. Maximum yield may be secured (90%) by the addition of 2% of cerium salt as catalyst [61]. This action of cerium salts was applied earlier in several industrial operations [62], [63].

SMITH and associates [64], on studying the structure of vitamin E, oxidized in 1941 derivatives of p-hydroxy-chroman and p-hydroxy-cumaran by cerium (IV) sulphate. On the basis of the observations of FURMAN [43] mentioned previously as carrying out the oxidation of hydroquinone to quinone by cerium (IV) sulphate, it was expected that oxidation will proceed only to the quinone state also with p-hydroxy-chroman and p-hydroxy-cumaran derivates. In the case of 2,2,5,7, 8-pentamethyl-6-hydroxy-chroman the process proceeded, as expected :

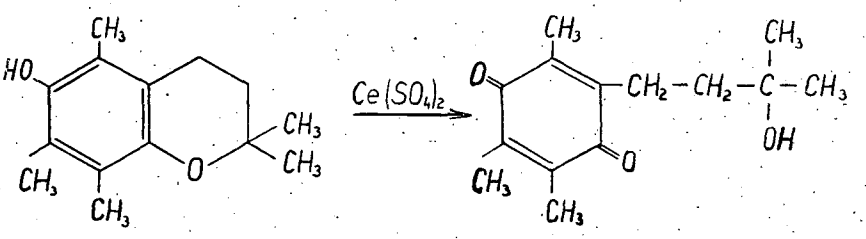

Fig. 2

On addition of the theoretically calculated quantities of 0,1—0,01 N $Ce(SO_4)_2$, the reaction proceeded quantitatively in 2—3 minutes in a medium of 50% ethanolic 1,0 N H_2SO_4.

A similar reaction was observed as well with the corresponding cumaran derivative:

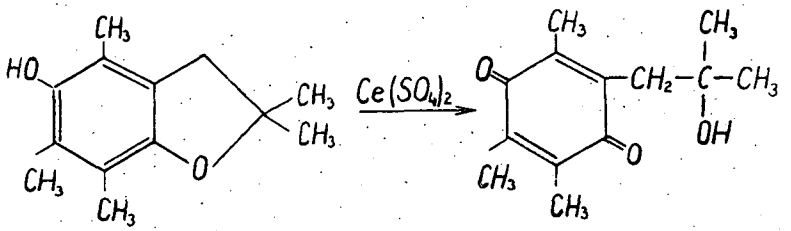

Fig. 3

Reactions conducted with homologues proved that on addition of the calculated quantities of $Ce(SO_4)_2$ the process proceeds only to the quinone state. This fact points to the specific oxidizing action of $Ce(SO_4)_2$ since oxidation processes of this type could not satisfactorily be conducted with any other oxidizing agent [65].

Oxidation with $Ce(ClO_4)_4$ was applied by HUSTON and associates for establishing the structure of compounds [66]. Namely, the position of the double bond in isomeric unsaturated esters was determined by oxydation the unsaturated esters to glycol esters and subjecting the product to oxidation by $Ce(ClO_4)_4$. Oxidizing 1-ethyl-2-methyl-2,3-dihydroxybutyric ethylate by $Ce(ClO_4)_4$, the following reaction was observed:

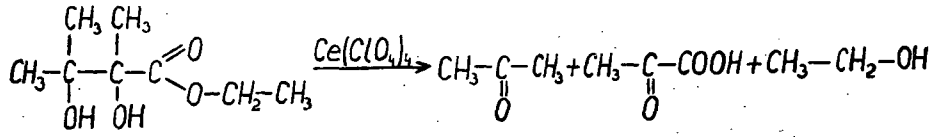

Fig. 4

The same method was applied by HUSTON [67] in another case with a similar aim:

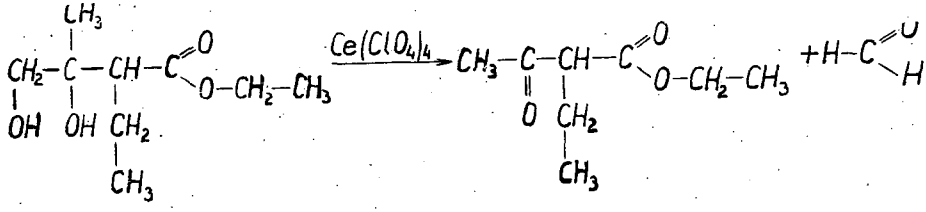

Fig. 5

The use of $Ce(ClO_4)_4$ in oxidation processes offers various advantages, due to its high redox potential [68]. This follows from the comparison of the experimental conditions of two different ways of determining glycerol. In order to attain complete oxidation, boiling for an hour is required in the presence of $Ce(SO_4)_2$ [69], whereas with $Ce(ClO_4)_4$ the same reaction proceeds at 50°C in only 15 minutes [70].

From the point of view of selectivity it must be noted that according to CUTHILL and ATKINS [71], tartronic acid forms quantitatively at the oxidation of glycerol.

* * *

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